THE COMPRESSIBILITIES OF THE ELEMENTS AND THEIR RELATIONS TO OTHER PROPERTIES

By T. W. Richards

WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY

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Eight years ago the compressibilities of thirty-five elements were determined at Harvard, in order to discover the relation of these compressibilities to one another and to other properties of these fundamental substances. All the values were referred to that of mercury, with the understanding that, although the compressibility of mercury was not at that time very well known, they could all be easily corrected to the true standard when more complete knowledge of this quantity had been attained.

This time now seems to have come. The recent research of Bridgman at high pressures and that of the author in conjunction with E. P. Bartlett at lower pressures have furnished such a consistent and convincing outcome that the compressibility of mercury is no longer in serious doubt. Accordingly, it is appropriate that the older results should be corrected to the true standard. Moreover, a better standard of pressure is now available, and the pressure gauges used in the early work have been very carefully compared with it, so that the older results can be corrected in this respect also.

The table below contains the corrected values of the compressibilities in question, together with new values for tungsten and tantalum, determined with the help of E. P. Bartlett, and of boron, determined with the help of J. H. Hodges.

The megabar (or megabarie) is chosen as the measure of pressure because this absolute unit bids fair to become the scientific standard of the future, being the pressure of one megadyne per square centimeter. It is almost 2% greater than the kilogram per square centimeter, and 1.3% less than the 'atmosphere.'

In addition to the compressibilities, the table records also several other properties, which will be shown to be more or less related. Many of these also have been determined at Harvard, but some are due to the work of others. Most of these latter are easily found in the literature; complete references would occupy far too much space for the present publication.

Compressibilities, Atomic Volumes, Densities, Melting Points, Coefficients of Expansion and Atomic Weights of a Majority of the Commonly Solid and Liquid Elements Between 100 and 500 Megabars (if the compressibility of mercury = 0.00000395).

	Average Compressibility at 20° (see above)	Atomic Volume	Density at 20°	Melting Point (absolute temp.)	Cubic Coefficient of Expansion × 100,000	International Atomic Weight (1914)
Lithium	9.0	13.1	0.534	453	19.	6.94
Boron	0.3	4.7	2.34	2800		11.0
Diamond	[0.7] (?)	3.4	3.51	Very high	0.3	12.00
Graphite	3.	5.4	2.26	Very high	7.2	12.00
Sodium	15.6	23.7	0.971	371	22.	23.00
Magnesium	2.9	13.3	1.74	927	7.8	24.32
Aluminium	1.47	10.1	2.60	930	7.2	27.1
Silicon	0.32	11.4	2.42	1733	2.3	28.3
Phosphorus, red	9.2	14.4	2.15	863		31.04
Phosphorus, white	20.5	16.6	1.82	317	36.	31.04
Sulphur	12.9	15.5	2.07	384	18.	32.07
Chlorine	[95] (?)	25.	1.42	171		35.46
Potassium	31.7	45.5	0.862	335	25.	39.10
Calcium	5.7	25.3	1.53	1073		40.07
Chromium	0.9	7.7	7.06	1823		52.0
Manganese	0.84	7.7	7.37	1533		54.93
Iron	0.60	7.1	7.85	1790	3.6	55.84
Nickel	0.43	6.7	8.7	1725	4.2	58.68
Copper	0.75	7.1	8.92	1356	5.0	63.57
Zinc	1.7	9.5	7.13	692	8.7 (?)	65.37
Arsenic	4.5	13.3	7.53	1073	1.6	74.96
Selenium	12.0	18.5	4.28	490	13.	79.2
Bromine	52.	25.1	3.12	266		79.92
Rubidium	40.	56.0	1.53	312	[30] (?)	85.45
Molybdenum	0.46	11.1	10.23	2773	1.1	96.0
Palladium	0.54	9.3	12.13	1822	3.8	106.7
Silver	1.01	10.3	10.5	1134	5.7	107.88
Cadmium	2.1	13.0	8.60	594	7.4	112.40
Tin	1.9	16.2	7.29	505	6.7	119.0
Antimony	2.4	17.9	6.71	903	3.3	120.2
Iodine	13.	25.7	4.94	386	25.0	126.92
Cesium	61.	71.0	1.87	301	[33] (?)	132.81
Tantalum	0.53	10.9	16.67	3123	2.3	181.5
Tungsten	0.27	9.6	19.23	3300(?)	1.1	184.0
Platinum	0.38	9.1	21.31	2020	2.7	195.2
Gold	0.66	10.2	19.24	1336	4.3	197.2
Mercury	3.95	14.8	13.55	234		200.6
Thallium	2.3	17.2	11.83	574	9.0	204.0
Lead	2.33	18.2	11.37	600	8.8	207.2
Bismuth	3.0	21.2	9.80	543	4.0	208.0

In the few cases where the compressibilities have been determined by others, especially by Grüneisen and Bridgman, the agreement with the results given above is good; and there is every reason to believe that these figures represent closely the true values of the constants in question. Therefore, they are worthy of further study, especially as regards their mutual relations and their relations to other properties.

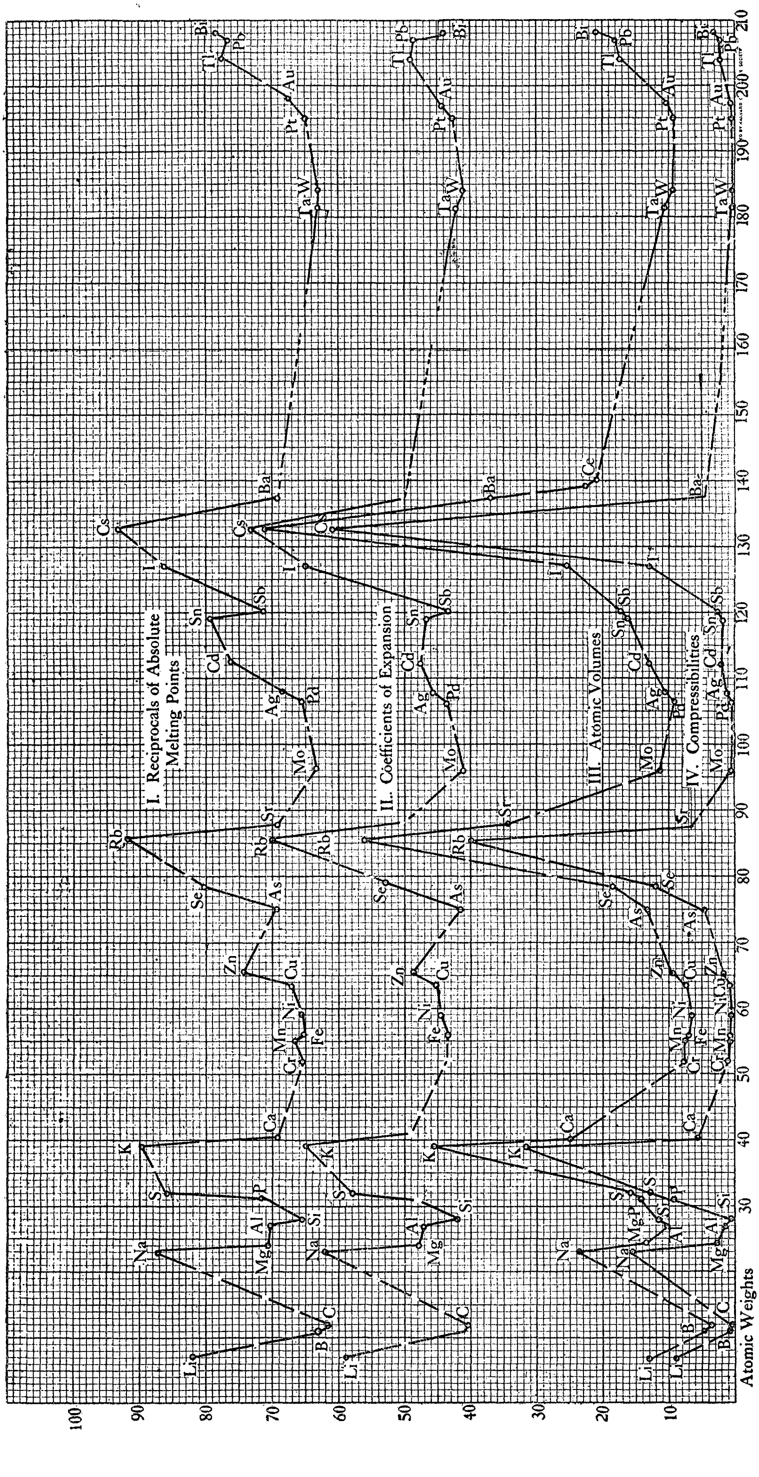

Diagram showing: I. Reciprocals of Absolute Melting Points; II. Coefficients of Expansion; III. Atomic Volumes; IV. Compressibilities of a Majority of the Commonly Solid and Liquid Elements between 100 and 500 Megabars.

Leaving out of consideration the behavior of the liquids, which doubtless is not fairly comparable with that of solids, we may compare these various quantities in parallel curves, each being plotted in relation to the increasing atomic weight. The accompanying diagram presents in the lowest line compressibilities; in the next above, atomic volumes; in the curve no. II, coefficients of expansion, and in the highest curve, the reciprocals of the absolute melting points.

That essential relations exist between these data cannot be doubted. In each case a maximum is seen to occur with the alkali metals; and although the rest of the curves are less similar, nevertheless, distinct connection is traceable. The compressibility curve is most like the atomic volume curve, and the coefficient of expansion curve most like that of the reciprocals of the melting points.

The attempt to find a mathematical relationship between these quantities is an interesting one. Such a relationship has already been sought by Grüneisen, Einstein, Debye, and others, upon the basis of a speculative theory, without much experimental support. With the wealth of data herewith presented, however, an empirical attempt is possible. It is soon evident on studying the figures that in cases where the melting points and atomic volumes are nearly similar, as, for example, in the cases of gold and silver, the denser substance is the less compressible. On the other hand, with similar density and melting point, as in the case of sodium or potassium, the substance with the greater atomic volume is the more compressible. Yet again, where the atomic volumes and densities are not very different, as in the case of sodium and calcium, the substance with the higher melting point has the lower compressibility. Taking account of these general tendencies, one sees that the equation should take this general form:

$$\text{Compressibility} = K\frac{f_1(V)}{f_2(D)f_3(T_m)}$$

in which K represents a constant, V the atomic volume, D the density, T_m the absolute melting point, f_1, f_2, f_3, various as yet undetermined functions.

The search for the nature of these respective functions is tedious and has not been carried very far; but the substitution in this equation of $K = 0.00021, f_1(V) = V, f_2(D) = D^{0.25}$ and $f_3(T_m) = (T_m - 50)$ gave results of about the right order with nearly all of the substances. For example, lithium is thus calculated to be 8 instead of 9, sodium, 15.6 (exactly its observed value), copper 0.66 instead of 0.75, silver 1.02 instead of 1.01, tungsten 0.29 instead of 0.27, etc. Some of the cal-

culated values, to be sure, deviated much more widely than this, but none is of entirely a different order from the truth. It is possible to show a necessary relationship between this empirical equation and the outcome of recent work by Grüneisen, and there is also some relationship between this equation and the well-known formula of Dupré, but the full discussion of these relationships would occupy more space than is available in the present publication. It may be noted, however, that the equation of Dupré is less satisfactory than the empirical equation just given as regards the elements, for density plays too large a rôle in the older expression. Moreover, the equation of Grüneisen is designed only for presumably monatomic elements, and it gives a negative (and therefore absurd) result for bismuth, showing that its range is more limited than that of the equation just mentioned.

No pretense is made, of course, that the empirical equation herewith communicated is a final statement of the relation of the quantities concerned. Nevertheless, because it gives the approximate order of magnitude of the compressibilities of widely different substances, one has a right to believe that the basis of the equation really refers to some of the more important tendencies which are at work.

Attention may be called to the fact that these relationships are in accord with those which would be expected from the prediction of the theory of compressible atoms. An atom much distended because of its internal makeup might be supposed to be highly compressible, and so might one much distended because not greatly pressed upon by outside cohesive pressure. Both of these tendencies would cause small density, and, accordingly, large atomic volume, and the second of these tendencies would add low melting point. Therefore, the general form of the equation is plausible.

A more complete discussion of the data and equation will soon be given in the *Journal of the American Chemical Society*.

Summary.—This paper records all the recent work on the compressibility of the elements performed at Harvard, reduced to the best available standard—the newly determined compressibility of mercury. It is pointed out that the reciprocals of the melting points are very closely associated with the coefficients of expansion, and that both of these properties seem to be essentially connected with atomic volume and compressibility. A preliminary empirical equation is proposed, which shows roughly the nature of this relationship.